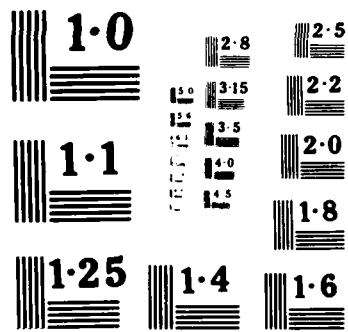


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Memory Effects on Infrared Adsorbate Spectra

by

Henk F. Arnoldus and Thomas F. George

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Departments of Chemistry and Physics  
State University of New York at Buffalo  
Buffalo, New York 14260

November 1987

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# MEMORY EFFECTS ON INFRARED ADSORBATE SPECTRA

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## ABSTRACT

A vibrational bond between an adsorbed atom and a crystal can absorb photons from a weak (probe) laser field (frequency  $\omega$ ). The line shape for this process is usually assumed to be a Lorentzian, which reflects that the kinetic coupling to the phonon reservoir is supposed to be a memoryless process. Due to the finite cutoff of the phonon dispersion relation (Debye frequency  $\omega_D$ ), this is not an accurate approximation if the transition frequency  $\omega_0$  between two levels of potential well is of the same order of magnitude as  $\omega_D$ . A finite memory-time reservoir theory is applied to the evaluation of the line shape, and two distinct properties were found. First, it is shown that the modified Lorentzian is identically zero for  $\omega > \omega_D$ , and then a memory-induced line at  $\omega = \omega_0 + \omega_D$  is predicted. The physical origin of these features is explained in terms of energy-conserving diagrams.

## ABSORPTION PROFILE

An atom is confined to the surface of a harmonic crystal by the van der Waals force. The potential depends on the atom-surface distance. Thermal motion of the crystal atoms makes this distance a dynamical variable, and the coupling provides an energy-exchange mechanism. Phonons in the crystal can be absorbed by the adsorbate, and the bond can emit energy into the crystal by excitation of a phonon. This process gives rise to thermal relaxation of the adsorbate density operator  $\rho(t)$  to a steady state  $\bar{\rho}$  (thermal equilibrium).

This system is irradiated by a low-intensity infrared laser, and the probability for the absorption of a photon as a function of its frequency  $\omega$  is indicated by  $I(\omega)$ . With  $d$  the dipole moment of the bond, projected on the laser-polarization direction,  $L$  the Liouvillian of the atom in the potential well and a suppression of an overall factor, a general expression for the absorption profile reads

$$I(\omega) = \text{Tr}d \left( \frac{i\omega}{\omega - L + i\Gamma(\omega)} ([d, \bar{\rho}] - iT(\omega)\bar{\rho}) \right) \quad (1)$$

In a Markov approximation the relaxation operator  $\Gamma(\omega)$  becomes  $\omega$ -independent, and the second term in round brackets,  $T(\omega)\bar{\rho}$ , disappears. For potential wells which have resonance frequencies of the order of  $\omega_D$ , a zero memory-time approximation, which leads to a Lorentzian line shape, cannot be justified.



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## MEMORY EFFECTS

Expression (1) for the profile pertains to any configuration of levels, any shape of the potential, and includes multiphonon transitions.<sup>2</sup> In order to study the effect of a finite reservoir response time we consider the case where the potential supports only two bound states, separated by  $\omega_0$ . In Fig. 1 we have plotted the line shape for the situation  $\omega_0 = 3\omega_D$ . The left peak comes from the term  $[d, \rho]$  in Eq. (1), which would be a Lorentzian around  $\omega_0$  in the Markov approximation. Due to the  $\omega$ -dependence of  $\Gamma(\omega)$  the line is cut off at  $\omega_D$ , and only the low-frequency wing at  $\omega < \omega_D$  remains. The line at the right-hand side is situated at  $\omega = \omega_0 + \omega_D$ , and it comes from the term proportional to  $T(\omega)$  in Eq. (1). Without a memory in the interaction, this line vanishes identically. We

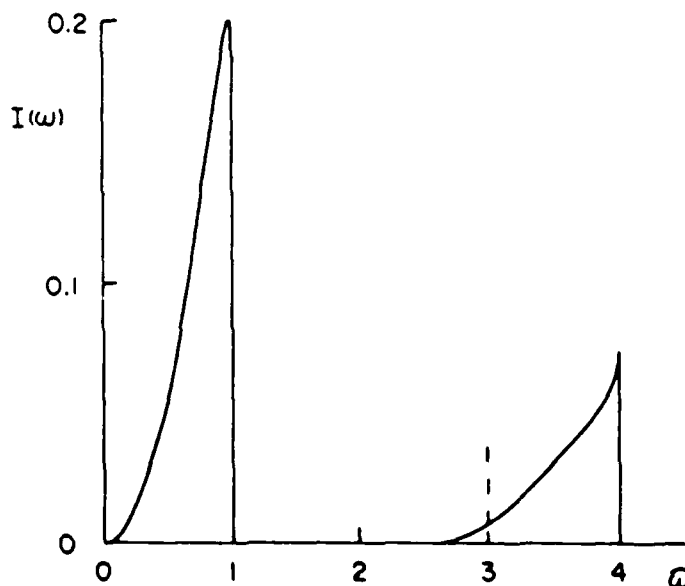


Figure 1. Typical absorption profile for a two-level system. Here,  $\hat{\omega} = \omega/\omega_D$  and the dotted line indicates the resonance frequency  $\omega_0 = 3\omega_D$ .

predict a memory-induced line at the sum frequency  $\omega_0 + \omega_D$ . In tracing back the mathematical origin of the operator  $T(\omega)$ , it appears that this term enters as a consequence of the fact that the density operator of the entire system does not factorize into a product of the crystal density operator times the adsorbate density operator.

The physical origin of the two lines in Fig. 1 can be illustrated with the diagrams from Fig. 2. Process (a) is

responsible for the line at  $\omega < \omega_D$ , which would usually be a Lorentzian. Since there are no phonons with a frequency larger than  $\omega_D$ , however, photon absorptions with  $\omega > \omega_D$  do not occur. Consequently, the line vanishes for  $\omega > \omega_D$ . Diagrams (b) and (c) explain the line around  $\omega \sim \omega_0 + \omega_D$ , and it follows immediately that the line must disappear for  $|\omega_0 - \omega| > \omega_D$ .

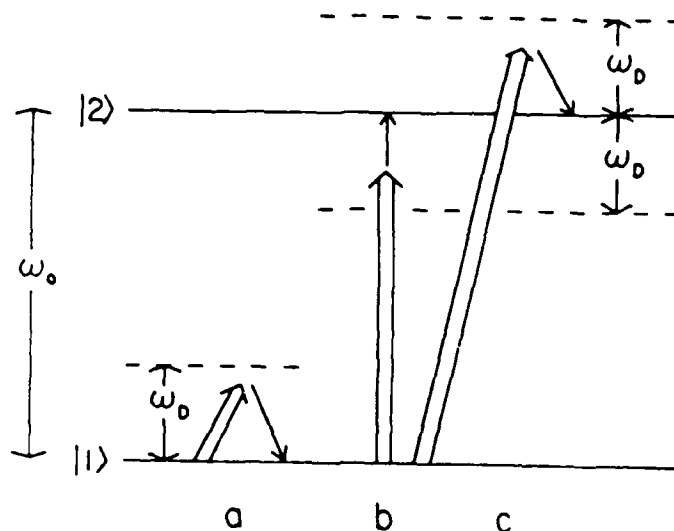


Figure 2. Transition diagrams which are responsible for the profile of Fig. 1. Double arrows indicate photons and single arrows are phonons.

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2. H. F. Arnoldus and T. F. George, Phys. Rev. B, submitted.

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